

USE OF DISPERSED CATALYSTS FOR COAL LIQUEFACTION

Albert S. Hirschon and R. B. Wilson Jr.

SRI International
Inorganic and Organometallic Chemistry Program
Menlo Park, California 94025

ABSTRACT

We have briefly explored the use of dispersed catalysts for conversion of an Illinois #6 into soluble products. We compared both supported and non-supported catalysts and found that the non-supported catalysts gives superior conversions. The non-supported catalysts were impregnated into the coal by use of either aqueous metal salts or organic solutions of organometallic complexes. The organometallic precursors were found to be exceptionally active and provide the greatest yields of toluene soluble products. Our key to effective dispersed catalysts is the use of a soluble sulfido complex that does not require high temperature activation.

INTRODUCTION

Although great progress has been made in converting coal to distillable liquids in high yields, the products are still not competitive with petroleum. A major problem is that under the severe conditions for bond-breaking during coal liquefaction, regressive reactions take place that produce char and coal liquids that are difficult to hydrotreat (1-6). For instance, phenolics are thought to polymerize into polymeric furans during the liquefaction process. In a similar manner, these coal liquids are high in nitrogen heterocycles. These heterocyclic oxygen and nitrogen containing molecules make coal liquids difficult to upgrade. In order to hydrotreat these materials such high temperatures and hydrogen pressures are required, that the valuable aromatic containing materials in the coal liquid are concurrently hydrogenated. In past work, we have concentrated on developing highly dispersed highly active catalysts to hydrotreat these coal liquids with the minimum consumption of hydrogen (7-11). In this work we look at the feasibility of using similar techniques to impregnate the coal with highly dispersed catalysts for improved liquefaction that give less regressive reactions.

Dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen donating solvent. An added advantage to these catalysts is that they can promote certain bond cleavage reactions during the liquefaction step. If they can aid in removing the heteroatoms, namely oxygen and nitrogen, during the early stages in coal liquefaction, then the detrimental regressive reactions would be minimized. Thus a better quality coal liquid product would be produced that would be easier and less expensive to hydrotreat.

Many workers have investigated non-supported high dispersion catalysts (12-21). Most work on dispersed catalysts has focused on metal salts such as ammonium molybdate or iron

sulfides, or oil soluble catalysts such as molybdenum naphthalate. Derbyshire et al. have conducted considerable research utilizing the $(\text{NH}_4)_2\text{MoO}_4$ and $(\text{NH}_4)_2\text{MoS}_4$ aqueous impregnation methods at low temperatures where they have shown that these dispersed catalysts can effectively utilize hydrogen to aid in subsequent conversions (13-15). The problem with most dispersed catalysts that have been tested is that they are only activated at high temperatures. For instance, molybdenum tetrathiolate decomposes to MoS_3 at low temperatures. However, the more active form is MoS_2 which is formed at much higher temperatures ($\geq 350^\circ\text{C}$) (22,23). In a similar manner, the molybdenum naphthalate needs to be transformed into MoS_2 . The importance of the correct stoichiometry has been emphasized by Montano et al. (24,25). They have suggested in work on iron sulfide catalysts that the pyrite (FeS_2) must be transformed to pyrrhotite, Fe_{1-x}S , ($0 < x < 0.125$) before it is catalytically active. Under coal liquefaction conditions, the sulfur must diffuse out of the pyrite to allow the transformation to occur. In contrast, when the precursor is $\text{Fe}(\text{CO})_5$, sulfur diffuses into the iron to form highly dispersed pyrrhotite.

Since we have been successful in increasing the activities of hydrotreating catalysts by use of organometallic precursors to form highly dispersed catalysts, we are very interested in using these same techniques for direct liquefaction catalysis (7-11). Our goals are to synthesize and test soluble complexes that are as close to the correct stoichiometry and structure of the active catalyst during the coal liquefaction. Thus we hope that our catalysts, since they do not require high temperature activation, will cause bond breaking reactions at lower temperatures than are currently possible with dispersed catalysts, and may therefore aid in reducing regressive reactions.

EXPERIMENTAL

The procedure for converting coal in tetralin is as follows. For the experiments involving aqueous pretreatment, the coal was pretreated by placing approximately 5 g of coal, 0.003 moles catalyst and 10 mL of distilled water in a 45-mL Parr bomb with a Teflon insert. The reactor was purged and pressurized with 500 psi of nitrogen and inserted into a preheated furnace for 30 min at 250°C . After the reactor had cooled, the insert was removed, and transferred into a centrifuge tube fitted with a screw cap. The aqueous layer was removed after centrifuging the mixture, and the pretreated coal washed twice with distilled water. The wet coal was mixed with 30 g of tetralin and then transferred to a 300 mL Autoclave Engineers MagneDrive autoclave.

All operations were conducted either in a nitrogen-filled glove bag or under a blanket of nitrogen, although brief exposure of the pretreated coal to air during the transfer could not be avoided. The autoclave was then purged and pressurized with 500 psi of hydrogen and heated at 400°C . The electric furnace could be raised or lowered by use of a remotely controlled jack. The typical heat-up time was 30 min. After 20 min reaction the heater was immediately lowered. The removal of the furnace gave a rapid cool down of about 100°C in about 5 minutes. After the reaction had cooled, the coal liquid and residue were taken up in tetrahydrofuran (THF). The THF was removed under reduced pressure and the residue taken up in toluene. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The toluene and residual tetralin were then removed from the TS under reduced pressure. The TS and TI fractions were then dried at 76°C for 12 h under vacuum (< 0.1 mm).

RESULTS AND DISCUSSION

This work was conducted in order to demonstrate that there is a correlation between our hydrogenolysis results and our liquefaction results due to the means of catalyst preparation. We feel the development of hydrotreating catalysts as important, since a good hydrogenolysis catalyst, should also be a good coal liquefaction catalyst. We have prepared these highly dispersed catalysts by impregnating homogeneous organometallic complexes on the support. The advantage of these

methods are that one can create "surface confined" highly dispersed, small particle sized catalysts throughout the support. In contrast, the conventional incipient wetness technique tends to cause large metal clusters to be formed, leaving a low surface area of active catalyst, and thus much less activities.

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The coal liquefaction experiments were conducted with a high ratio of tetralin to coal (6 to 1). Therefore, we would expect that the effect of the catalyst in terms of providing a reducing environment or forming an active solvent should be minimized. Thus, any differences we see in conversions should primarily reflect the effect of the catalyst promoting bond breaking reactions. (although one could argue that the catalyst is producing low concentrations of reactants derived from the solvent that are actually producing the bond breaking).

Table 2 lists some of our results for conversion of coal into toluene soluble material. The conversion is calculated from the insoluble material corrected for the ash content. Molybdenum tetrathiolate was chosen since it is an excellent hydrogenation and liquefaction catalyst precursor and also can be used to form mixed metal sulfide clusters which may be used as hydrogenolysis catalysts. One question to be addressed for the water soluble molybdenum salt was the optimum method of preparation. We thought that the ideal way to impregnate the coal is the mix the coal in an aqueous solution of the thiomolybdate salt, and heat the solution at 250°C for 30 min. This hot aqueous impregnation is thought to swell the coal, and thus allow better impregnation with the aqueous catalyst. Experiments 1-3 in Table 2 show the results after this aqueous impregnation. In the first experiment, the coal was impregnated and then dried under vacuum at 76°C to remove the water. In the second experiment, the coal was impregnated, centrifuged to remove the excess water, and the immediately placed in the autoclave. In the third experiment, the molybdate salt was dissolved in 4 mL of water, and added to the coal with tetralin, without any impregnation. As shown in this table, experiment 1 gave a low conversion (41%), compared to experiments 2 and 3 (51%). When the coal was dried, the molybdenum catalyst may have become larger in cluster size or allowed crosslinking in the coal matrix to occur.

For comparison, we chose two organometallic molybdenum dimers. A sulfido complex, $\text{Cp}_2\text{Mo}_2(\mu\text{-SH})_2(\mu\text{-S})_2$, and a molybdenum acetate dimer, $\text{Mo}_2(\text{OAc})_4$. As shown in experiments 4 and 5, respectively, the sulfido dimer provides a much higher conversion than the aqueous impregnation methods, (61% compared to $\approx 50\%$), and also a higher conversion than the non-sulfided $\text{Mo}_2(\text{OAc})_4$ catalyst (55%).

CONCLUSIONS

We view this enhancement with the organometallic complexes as the ability to be better dispersed than the aqueous impregnation techniques, in a similar manner as demonstrated in our hydrotreating results. The highest activity with the sulfido complex, we believe, is because the catalyst was impregnated in a highly active form, and thus does not require subsequent activation during the liquefaction step. Thus the advantages of our methods are (1) the catalyst can be readily impregnated into the coal and (2) we can design a catalyst such that it transforms directly into the correct stoichiometry for the active form of the catalyst. In future work we hope to investigate the scope of these highly active catalysts, and prepare soluble mixed metal clusters which should enhance the liquefaction of coal still further.

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Table 1
TURNOVER FREQUENCIES FOR QUINOLINE HDN^a

Catalyst	Precursor	TF ^b		
		THO	PCH	PB
NiMo	Conv	67.4	8.2	0.3
NiMo(OM)	Mo ₂ (OAc) ₄	41	3.4	0.5
NiMo(OM)	Mo ₂ (allyl) ₄	111	26.5	1.4

^aReaction of 10 mL of 0.0197 M quinoline in n-hexadecane and 0.100 g catalyst at 350°C and 500 psig H₂.

^bTF - moles reactant or product/total moles metal/h

Table 2
CATALYZED TETRALIN CONVERSIONS^a

No	Pretreatment	% TS ^b
1	MoS ₄ /Dried ^c	41
2	MoS ₄ /4 mL ^d	52
3	MoS ₄ /Wet ^e	52
4	Cp ₂ Mo ₂ (μ-SH) ₂ (μ-S) ₂	61
5	Mo ₂ (OAc) ₄	56

^aReaction conducted in 300-mL autoclave of 5 g coal in 30 g of tetralin and 500 psi H₂ at 400°C/20 min.

^bSolubility based on wt % insoluble material, corrected for ash.

^cCoal was dried at 76°C under vacuum after aqueous molybdenum impregnation.

^dMolybdenum was dissolved in water (4 mL) added to the coal/tetralin mixture.

^eCoal was impregnated with aqueous molybdenum, and transferred to the autoclave while wet.